XV. "Researches on the Phosphorus-Bases."—No. XIV. Action of Triethylphosphine on the Substitution-compounds of Marsh-Gas. By A. W. HOFMANN, LL.D., F.R.S. Received May 24, 1861.

The formation of diatomic bases by the action of triethylphosphine on dibromide of ethylene, very naturally suggested the idea of studying the deportment of the phosphorus-base with the numerous brominated derivatives of the ethylene-series discovered by Cahours, and lately examined again by A. Lennox. All these compounds act indeed with extraordinary energy upon triethylphosphine; the products, however, of these reactions are far from exhibiting, with regard to the compounds from which they originate, the simplicity and intimacy of relation which theoretical speculation, based on the observation of the action of dibromide of ethylene, might lead us to expect. Most of the brominated substitution-products are apt to lose either bromine or hydrobromic acid, the bromides respectively of triethylphosphine and of triethylphosphonium being formed, together with secondary phosphonium-compounds of subordinate theoretical interest which I have not investigated in detail.

It still remained to study the deportment of the phosphorus-bases with chlorine- and bromine-compounds of simpler constitution. Hoping to obtain more characteristic results in this direction, I was led to submit the compounds which are formed by the action of triethylphosphine on some of the substitution-products of marsh-gas to a more minute examination.

The action of chlorine upon marsh-gas has been the subject of an important investigation by Regnault, who has shown that the gradual substitution of chlorine for hydrogen gives rise to the following series.

Marsh-gas	$C\,H_4$	Tetrahydride of Carbon.
Monochlorinated marsh-gas	$C\,H_3\,Cl$	Chloride of Methyl.
Dichlorinated marsh-gas	$C\,H_2\,Cl_2$	Dichloride of Methylene.
Trichlorinated marsh-gas	$C\,H\,Cl_3$	Trichloride of Formyl.
Tetrachlorinated marsh-gas	$C\,Cl_4$	Tetrachloride of Carbon.

I was anxious to ascertain whether these four chlorinated derivatives, when submitted to the action of triethylphosphine, would fix respectively 1, 2, 3 and 4 molecules of the phosphorus-base, giving

rise to the formation of mono-, di-, tri-, and tetra-phosphonium-compounds, the composition of which was pointed out in advance by theory.

Some of the products which are generated by the action of the chlorinated substitutes of marsh-gas are already known. Chloride of methyl fixes one molecule of triethylphosphine, giving rise to the chloride of methyl-triethylphosphonium,

$$CH_3Cl + (C_2H_5)_3P = [(CH_3)(C_2H_5)_3P]Cl,$$

which in combination with dichloride of platinum was examined several years ago by Cahours and myself.

The product which is generated by the action of chloroform on triethylphosphine is likewise known. I have shown that chloroform is capable of fixing three molecules of phosphorus-base, producing the trichloride of formyl-nonethyltriphosphonium,

$$(CH)'''Cl_3 + 3[(C_2H_5)_3P] = \left[(CH)''' \begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3P \\ (C_2H_5)_3P\end{matrix}\right]'''Cl_3.$$

A short account of this substance has been already communicated to the Royal Society *.

It remained therefore only to examine the deportment of triethylphosphine with the second, and likewise with the fourth of the chlorinated substitution-products. Dichloride of methylene, the product obtained by the action of chlorine on chloride of methyl, acts with considerable energy on triethylphosphine. Digestion of the mixture for a few hours at a temperature of 100° in sealed tubes, suffices to accomplish the reaction. The products vary considerably, according to the proportion in which the two agents are mixed. One molecule of dichloride of methylene and one molecule of triethylphosphine give rise to the formation of the beautifully crystallized chloride of chloromethyl-triethylphosphonium,

$$CH_2Cl_2 + (C_2H_5)_3P = [(CH_2Cl)(C_2H_5)_3P]Cl.$$

This chloride forms with dichloride of platinum a double salt, beautifully crystallized in needles, rather difficultly soluble in water, which contains

$$[(CH_2Cl)(C_2H_5)_3P]Cl, PtCl_2.$$

The chloromethylated triethylphosphonium-salt is capable of fixing a second equivalent of triethylphosphine. The crystalline mass

* Proceedings, vol. x. p. 189.

obtained in this manner is obviously the dichloride of methylene-hexethyldiphosphonium,

$$[(CH_2Cl)(C_2H_5)_3P]Cl+(C_2H_5)_3P=\left[(CH_2)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2.$$

I have not succeeded in seizing the dichloride in a state fit for analysis, since this compound cannot be brought in contact with water without undergoing immediate decomposition; but I have been able to trace the diatomic compound in its products of decomposition. The solution of the dichloride is not precipitated by dichloride of platinum, but, on evaporation, orange-yellow, well-developed octohedra are deposited, which are the platinum-salts of methyltriethylphosphonium. The mother-liquor of the octohedra furnishes the six-sided tables of the platinum-salt of triethylphosphine.

The following equation represents the transformation of the dichloride of the diphosphonium under the influence of water,

$$\left[(CH_2)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2+\left.\begin{matrix}H\\H\end{matrix}\right\}O=[(CH_3)(C_2H_5)_3P]Cl+(C_2H_5)_3PO+HCl.$$

It is thus seen that the diatomic compounds of the methylene-series undergo, even in the form of salts and at the common temperature, a change which in the ethylene-series is observed only with the free bases and under the influence of a high temperature. When hydrate of ethylene-hexethyldiphosphonium is heated, hydrate of tetrethylphosphonium and oxide of triethylphosphine are prominent among the products of decomposition,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]''\\H_2\end{matrix}\right\}O_2=\left.\begin{matrix}[(C_2H_5)_4P]\\H\end{matrix}\right\}O+(C_2H_5)_3PO.$$

Di-iodide of methylene (obtained by the action of heat upon iodoform) imitates in every respect the deportment of the chlorine-compound with triethylphosphine. The dibromide, on the other hand, which is formed by the action of bromine upon the di-iodide, acts in a perfectly different manner. I propose to examine this reaction in a subsequent communication.

The action of tetrachloride of carbon, CCl_4, on triethylphosphine gives rise to changes resembling in many respects the transformations which I have described. On submitting tetrachloride of carbon to the action of triethylphosphine, I was surprised to find that the chloride, which resists with such pertinacity the influence of the

most powerful agents, is attacked with tremendous energy. A drop of triethylphosphine falling into tetrachloride of carbon hisses like water poured upon red-hot iron. It is necessary to operate in vessels filled with carbonic acid gas, to prevent the inflammation of the phosphorus-base, and to accomplish the mixing gradually by using a dropping apparatus. Or the force of the reaction may be diminished by employing the two liquids dissolved in anhydrous ether. Here also the relative proportions in which the two compounds are brought in contact, influence in a measure the result of the reaction; the presence of moisture likewise is apt to change materially the nature of the transformation.

Obtained in presence or in absence of ether, the product of the reaction is a white crystalline exceedingly deliquescent substance. Submitted to the action of water, the crystals dissolve with powerful evolution of heat, giving rise to an intensely acid solution. On adding dichloride of platinum to this liquid, a crystalline precipitate, very difficultly soluble in water, but soluble in boiling concentrated hydrochloric acid, is thrown down, which, on analysis, was found to be the formylated nonethyltriphosphonium-salt,

$$C_{19}\,H_{46}\,P_3\,Pt_3\,Cl_9 = \left[\begin{matrix} & (C_2\,H_5)_3\,P \\ (C\,H)''' & (C_2\,H_5)_3\,P \\ & (C_2\,H_5)_3\,P \end{matrix}\right]'''\,Cl_3,\ 3\,Pt\,Cl_2,$$

which was identified by conversion into the corresponding iodide.

The mother-liquor of the triatomic platinum-salt gave, on evaporation, orange-yellow octohedra containing

$$C_7\,H_{17}\,PPt\,Cl_4 = [(C\,H_2\,Cl)(C_2\,H_5)_3\,P]\,Cl,\ Pt\,Cl_2.$$

The liquid from which this salt had been deposited, furnished, on further evaporation, considerable quantities of oxide of triethylphosphine, which was identified in the form of the beautiful iodide-of-zinc-compound,

$$(C_2\,H_5)_3\,P\,O,\ Zn\,I$$

described in one of my former Notes.

The interpretation of these phenomena presents no difficulties. The existence of the hydrogenated radicals (C H) and (C H_2 Cl) in the solution of the products of the action of C Cl_4 on $(C_2\,H_5)_3\,P$, unmistakeably shows that these substances are only secondary products, which owe their origin to the action of water upon the

compounds formed directly by the union of triethylphosphine with tetrachloride of carbon. The chemical action of the water is proved, moreover, by the disengagement of heat to which I have alluded, and by the existence of a large quantity of free hydrochloric acid in solution.

I have not succeeded in obtaining the direct product of the action of tetrachloride of carbon on triethylphosphine in a state fit for analysis; the extraordinary deliquescence of the product, and the impossibility of touching it with a solvent without decomposing it, have frustrated my efforts. But here again, exactly as in the case of the diphosphonium-compound, the study of the products of decomposition leaves no doubt about the nature of the reaction; it shows that the direct product of the action of tetrachloride of carbon on triethylphosphine is a mixture of two chlorides, viz.—

Tetrachloride of carbo-dodeca-ethyltetraphosphonium,

$$C_{25}\,H_{60}\,P_4\,Cl_4 = \left[C^{iv} \begin{matrix} (C_2\,H_5)_3\,P \\ (C_2\,H_5)_3\,P \\ (C_2\,H_5)_3\,P \\ (C_2\,H_5)_3\,P \end{matrix} \right]^{iv} Cl_4$$

and trichloride of chlorocarbo-nonethyltriphosphonium,

$$C_{19}\,H_{45}\,P_3\,Cl_4 = \left[(C\,Cl)''' \begin{matrix} (C_2\,H_5)_3\,P \\ (C_2\,H_5)_3\,P \\ (C_2\,H_5)_3\,P \end{matrix} \right]''' Cl_3.$$

The tetraphosphonium-compound, submitted to the action of water, gives rise to the formation of the formylated triphosphonium-salt, oxide of triethylphosphine and hydrochloric acid,

$$\left[C^{iv} \begin{matrix} (C_2H_5)_3\,P \\ (C_2H_5)_3\,P \\ (C_2H_5)_3\,P \\ (C_2H_5)_3\,P \end{matrix} \right]^{iv} Cl_4 + \left.\begin{matrix} H \\ H \end{matrix}\right\} O = \left[(CH)''' \begin{matrix} (C_2H_5)_3P \\ (C_2H_5)_3P \\ (C_2H_5)_3P \end{matrix} \right]''' Cl_3 + (C_2H_5)_3PO + HCl.$$

The chlorocarbonated triphosphonium-salt furnishes with water the chloromethylated monophosphonium-compound, oxide of triethylphosphine and hydrochloric acid,

$$\left[(CCl)''' \begin{matrix} (C_2H_5)_3P \\ (C_2H_5)_3P \\ (C_2H_5)_3P \end{matrix} \right]''' Cl_3 + 2\left.\begin{matrix} H \\ H \end{matrix}\right\} O = [(CH_2Cl)\,(C_2H_5)_3P]\,Cl + 2\,[(C_2\,H_5)_3PO] + 2HCl$$

The experiments described in this Note, together with those which I have communicated to the Royal Society on a former occasion, prove that the number of molecules of triethylphosphine which, under

favourable circumstances, can be fixed by the chlorinated derivatives of marsh-gas, is determined by the number of chlorine-equivalents which these substances contain. These bodies need not, however, assimilate the maximum quantities of triethylphosphine represented by these numbers. Thus dichloride of methylene is capable of fixing either one or two molecules of phosphorus-base, the formation of the ephemeral diatomic base being invariably preceded by that of the more stable chloromethylated monophosphonium-compound. Similar phenomena are observed in the action of chloroform and tetrachloride of carbon. The compounds which I have described as resulting from these reactions, are not the only products; by changing the relative proportions of the agents, a number of chlorinated phosphonium-bases are formed so much resembling each other, that I have failed in separating them. Nevertheless, by determining the amount of chlorine and platinum in the mixed platinum-salts obtained from these mixtures, I had no difficulty in recognizing the principle involved in their formation. These substances stand to the final products of the reaction of the triphosphonium and tetraphosphonium-series in relations similar to those which obtain between the chloromethylated monophosphonium and the ephemeral diphosphonium-compound.

The results of these inquiries may be condensed in a few formulæ.

The chlorinated derivatives of marsh-gas exhibit, in their deportment with the phosphorus-bases, the characters of hydrochloric acid. The monochlorinated product has the saturating capacity of one molecule of hydrochloric acid, the dichlorinated product of one or two molecules, the trichlorinated of 1, 2 or 3 molecules, the tetrachlorinated product, lastly, of 1, 2, 3 or 4 molecules:

$$C\,H_3\,Cl = (C\,H_3)'\ \ Cl.$$
$$C\,H_2\,Cl_2 = (C\,H_2\,Cl)'\ Cl = (C\,H_2)''\ \ Cl_2.$$
$$C\,H\ \ Cl_3 = (C\,H\ \ Cl_2)'\ Cl = (C\,H\,Cl)''\ Cl_2 = (C\,H)'''\ Cl_3.$$
$$C\ \ \ Cl_4 = (C\,Cl_3)'\ \ Cl = (C\,Cl_2)''\ \ Cl_2 = (C\,Cl)'''\ Cl_3 = C^{iv}\,Cl_4.$$

The action of chloride of methyl on triethylphosphine produces only one salt; that of dichloride of methylene produces two; chloroform is capable of producing three; and tetrachloride of carbon, four salts.

Monochlorinated Marsh-gas.

Monatomic compound ...... $[(C\,H_3)\,(C_2\,H_5)_3\,P]\,Cl.$

Dichlorinated Marsh-gas.

Monatomic salt	$[(\mathrm{C\,H_2\,Cl})'\,(\mathrm{C_2\,H_5})_3\,\mathrm{P}]'\,\mathrm{Cl}.$
Diatomic salt	$\left[(\mathrm{C\,H_2})''\ \begin{matrix}(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\end{matrix}\right]''\mathrm{Cl_2}.$

Trichlorinated Marsh-gas.

Monatomic salt	$[(\mathrm{C\,H\,Cl_2})'\,(\mathrm{C_2\,H_5})_3\,\mathrm{P}]\ \mathrm{Cl}.$
Diatomic salt	$\left[(\mathrm{C\,H\,Cl})''\ \begin{matrix}(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\end{matrix}\right]''\mathrm{Cl_2}.$
Triatomic salt........	$\left[(\mathrm{C\,H})'''\ \begin{matrix}(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\end{matrix}\right]'''\ \mathrm{Cl_3}.$

Tetrachlorinated Marsh-gas.

Monatomic salt	$[(\mathrm{C\,Cl_3})'\ \ (\mathrm{C_2\,H_5})_3\,\mathrm{P}]\ \mathrm{Cl}.$
Diatomic salt	$\left[(\mathrm{C\,Cl_2})''\ \begin{matrix}(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\end{matrix}\right]''\mathrm{Cl_2}.$
Triatomic salt........	$\left[(\mathrm{C\,Cl})'''\ \begin{matrix}(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\end{matrix}\right]'''\ \mathrm{Cl_3}.$
Tetratomic salt	$\left[\mathrm{C^{iv}}\ \begin{matrix}(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\\(\mathrm{C_2\,H_5})_3\,\mathrm{P}\end{matrix}\right]^{\mathrm{iv}}\ \mathrm{Cl_4}.$

June 20, 1861.

Major-General SABINE, R.A., Treasurer and Vice-President, in the Chair.

In accordance with the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

Dr. Heinrich Debus, Mr. Campbell De Morgan, Dr. Thomas A. Hirst, Professor James Clerk Maxwell, Dr. Edmund Alexander Parkes, Professor William Pole, Mr. Philip Lutley Sclater, Professor Henry John Stephen Smith, and Dr. Thomas Thomson, were admitted into the Society.

The following communications were read:—